

First steps towards dissolution of NaSO_4^- by water[†]

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Received 12th July 2006, Accepted 31st July 2006

First published as an Advance Article on the web 7th August 2006

DOI: 10.1039/b609941f

$\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) clusters have been generated in the gas phase as model systems to simulate the first dissolution steps of sulfate salts in water; photoelectron spectroscopy and theoretical calculations indicate that the first three water molecules strongly interact with both Na^+ and SO_4^{2-} , forming a three-water solvation ring to start to pry apart the $\text{Na}^+\text{SO}_4^{2-}$ contact ion pair.

Detailed knowledge of how polar molecules are dissolved in a solvent is essential to understanding the chemistry taking place in salt solutions and the fate and transport of environmental pollutants. Despite significant theoretical efforts directed at elucidating the dissolution of simple diatomic salt molecules¹⁻⁴ and acids,⁵⁻⁷ the molecular processes and the initial steps of dissolution are not well understood. Experimental techniques have been developed to probe the dissolution processes with hydrated clusters of diatomic molecules, such as NaI or HBr , by detecting chemical changes as a function of the number of water molecules.⁸⁻¹⁰ Very recently, the hydration energies and the dissolution processes of charged salt clusters, such as $(\text{NaX})_n\text{Na}^+$ ($\text{X} = \text{Cl}, \text{I}$), have been reported.^{11,12} It has been suggested that only a few waters are required to form stable and characteristic solvent separated ion pairs (SSIP), *i.e.* ~ 5 for HBr ,⁸ ~ 6 for NaCl and Na_2I^+ ,^{2,12} which is qualitatively consistent with simple saturation concentration data in the respective bulk solutions.⁹ Here we examine the microdissolution of a complex salt, Na_2SO_4 . Sulfate is ubiquitous in solids, solutions, and atmospheric aerosols.¹³⁻¹⁵ Molecular level information about the dissolution of sulfate should prove valuable in understanding its behavior and chemistry in the bulk phases and in complex environments. The SO_4^{2-} dianion allows us to produce contact ion pairs (CIP), such as MSO_4^- ($\text{M} = \text{alkali atoms}$),¹⁵ which provide a convenient handle for detection in the gas phase. Both CIP and SSIP are present in sulfate solutions depending on the concentration.^{16,17} Our goal is to follow the microhydration of CIP toward the onset of conversion to SSIP as a function of water in hydrated clusters, $\text{NaSO}_4^-(\text{H}_2\text{O})_n$.

We produced $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ clusters from a 10^{-3} M Na_2SO_4 solution in a $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ mixed solvent using electrospray ionization and studied their structures and energetics by photoelectron spectroscopy (PES) and *ab initio* calculations. The electrospray ionization-PES apparatus has been described in detail before.¹⁸ Our previous studies^{13,19,20} showed that $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters were the dominating species from our electrospray ionization source with relatively high water vapor around. However, under relatively dry conditions, bare NaSO_4^- and $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ with $n = 1, 2$ were generated, but no $n = 3, 4$ species could be observed (Fig. 1, top). Tuning the Na_2SO_4 concentration and the partial water pressure in the electrospray ionization source, we were able to produce $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ with n up to 4 (Fig. 1, bottom). The source conditions and the solution concentration were carefully tuned to optimize each species before recording its PES spectrum. We observed clusters with $n > 4$, but the mass intensities of the larger clusters were too weak to allow us to take their PES spectra.

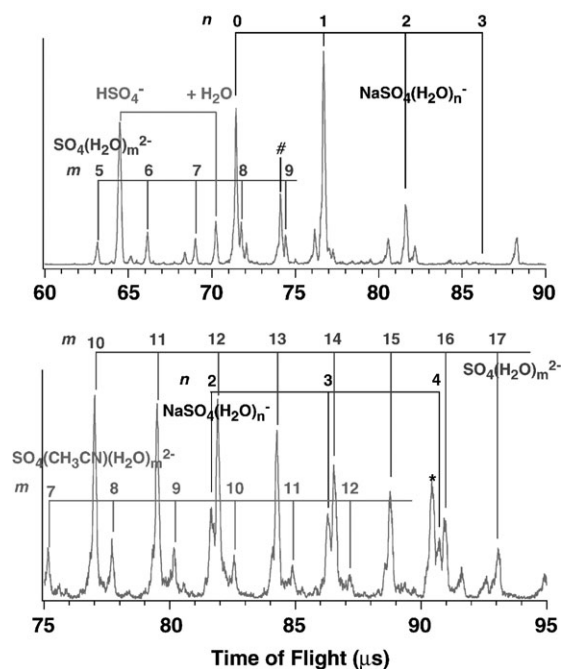


Fig. 1 Mass spectra of $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) under dry (top) and relatively humid (bottom) electrospray ionization conditions. All major species are labeled. The mass peak with '*' is an unidentified impurity, and the one labeled with '#' is the $(\text{NaSO}_4)_2^{2-}(\text{H}_2\text{O})_1$ dianion (see ref. 21).

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[†] Electronic supplementary information (ESI) available: Photoelectron spectra of other related species. See DOI: 10.1039/b609941f

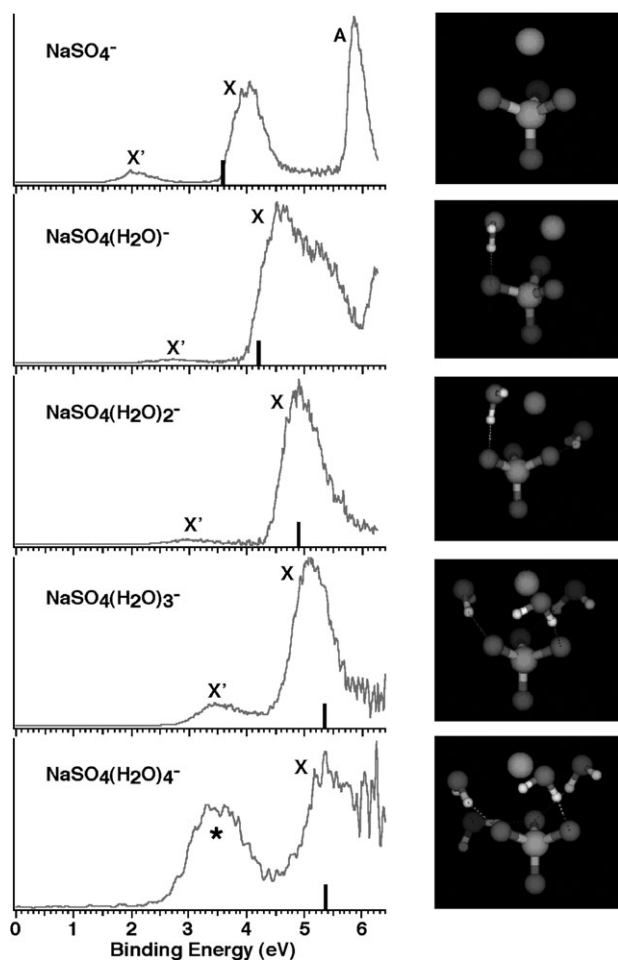


Fig. 2 PES spectra of $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) at 193 nm (6.424 eV) and their optimized structures. Calculated VDEs are shown as vertical bars. The feature noted with "*" for the $n = 4$ cluster is due to an impurity (see Fig. 1 and ESI†).

The PES spectra of $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) recorded at 193 nm (6.424 eV) are shown in Fig. 2. The bare NaSO_4^- spectrum, which has been reported before,¹⁵ shows three well-separated and rather broad features (labeled X', X and A), and is presented here as a reference. The weak X' band is due to detachment from the $(\text{NaSO}_4)_2^{2-}$ dimer, which has the same m/z ratio as the monomer.¹⁵ The X and A features are assigned as due to detachment from the HOMO (t_1) and HOMO-1 (t_2) of SO_4^{2-} . Upon adding water molecules, the binding energies of all features increase systematically due to solvent stabilization of the anion. The A band was no longer accessible for $n > 1$.

The incremental increase of electron binding energies, defined as $\text{VDE}(n) - \text{VDE}(n - 1)$, where $\text{VDE}(n)$ is the vertical detachment energy measured from the peak of X for $\text{NaSO}_4^-(\text{H}_2\text{O})_n$, is 0.5, 0.4, 0.2, and 0.2 eV for $n = 1-4$, respectively. Because of the broadness of the X peaks, the estimates of the VDEs are rather rough. The X' feature in each spectrum is due to the corresponding $(\text{NaSO}_4)_2^{2-}(\text{H}_2\text{O})_{2n}$ dimer clusters.²¹ The strong low binding energy band centered at 3.5 eV (denoted as *) in the spectrum of $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ is due to contamination by an unknown species 1 m/z below $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ (Fig. 1). This contaminant could not be

completely eliminated because it is too close to the $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ mass peak to allow a clean mass selection. We confirmed that the contaminant has negligible contributions to the observed 5.3 eV feature (X) assigned for $\text{NaSO}_4^-(\text{H}_2\text{O})_4$.²²

To obtain detailed molecular structures and understand how water interacts with NaSO_4^- we performed *ab initio* calculations. We computed VDEs to compare with the experimental data. We used the Gaussian03 package.²³ For each $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ cluster we performed geometry optimization without pre-imposed symmetry. For the larger clusters we started from several different chemically reasonable structures in order to locate the global minimum. The VDE was calculated as the difference between the energy of the optimized anionic structure and that of the corresponding neutral at the anionic geometry. In the case of neutral species, which are open-shell systems, projected MP2 energies were considered.²⁴

The first water was found to bind between the SO_4^{2-} and Na^+ parts of the ion-pair. This water molecule is orientated in such a way that it binds both to SO_4^{2-} and Na^+ by optimizing the O-H...O H-bond and water O...Na interaction (Fig. 2). The association of the first water is very strong, with a binding energy of 29.6 kcal mol⁻¹ (Table 1). The second and third water molecules behave in a similar way, each forming one O-H...O H-bond with a sulfate O atom while the water O atom points towards Na^+ . The binding energies are also large, 27.1 and 21.7 kcal mol⁻¹ for the two waters of the $n = 2$ cluster, and 21.1 kcal mol⁻¹ for each water molecule of the $n = 3$ cluster (Table 1). Note, that these binding energies, which are corrected for the basis set superposition error, correspond to the removal of a single water molecule from the cluster without any other geometry changes. Thus, the first three waters occupy all three O sites of SO_4^{2-} facing Na^+ , forming a solvation ring between Na^+ and SO_4^{2-} and separating the two ions from their tight CIP form. The Na-S distance gradually increases from 2.50 Å in the bare CIP to 2.71, 2.81, and 2.84 Å upon adding 1 to 3 water molecules, respectively (Table 1). Such a three-water solvation ring structure was also proposed in previous studies of dissolution of diatomic salt and acids.^{5,6} When the fourth water is added, it has to bind elsewhere. The best site for this water is next to SO_4^{2-} but further from Na^+ (Fig. 2). The binding of this water is significantly lower than that of the first three H_2O , dropping to ~16 kcal mol⁻¹, but it still results in an additional increase of the Na-S distance to 2.93 Å.

The calculated VDE of NaSO_4^- is 3.58 eV (Table 1), comparable with our previous study.¹⁵ The calculation also

Table 1 Calculated vertical detachment energies (VDE's), binding energies of individual water molecules, and Na-S distances for $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) at MP2/aug-cc-pvdz level with projected MP2 energies considered (see text)

n	VDE/eV	$E_{\text{bind}}/\text{kcal mol}^{-1}$	$R_{\text{Na-S}}/\text{Å}$
0	3.58	—	2.50
1	4.20	29.6	2.71
2	4.91	27.1; 21.7	2.81
3	5.34	21.1; 21.1; 21.1	2.84
4	5.37	23.2; 20.9; 18.9; 16.2	2.93

predicted successive increases of the VDE's, by 0.62 eV for the first water, 0.71 eV for the second, 0.43 eV for the third, and 0.03 eV for the fourth water. The calculated VDEs are compared with the experimental data in Fig. 2 as vertical bars. Good agreement is obtained between the calculated VDEs and the experiment, providing credence to the solvated structures.

The obtained solvated structures for $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) have direct connections with the processes occurring in concentrated sulfate solutions. The CIP and SSIP were proposed to coexist in solutions from previous computational and experimental investigations.^{16,17} Because of the unique framework of NaSO_4^- , the first three water molecules behave both as acid (donating H to sulfate) and base (O of water interacting with Na^+). The formed three-water solvation ring begins to separate the cation from the anion, which is a manifestation of the initial steps of dissolution. Additional water molecules further destabilize the sodium-sulfate bond, which will eventually lead to the formation of a SSIP. In our future work we will attempt to establish the number of water molecules necessary to solvent separate the two ions.

Acknowledgements

The experimental work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Sciences Division and was performed at the EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle. Supports from the Czech Ministry of Education (grants LC512 and ME644) and from the US-NSF (grants CHE-0431312 and CHE-0209719) for the theoretical work are gratefully acknowledged.

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- L. S. Wang, C. F. Ding, X. B. Wang and S. E. Barlow, *Rev. Sci. Instrum.*, 1999, **70**, 1957. Briefly, the apparatus is equipped with an electrospray ionization source, a time-of-flight (TOF) mass spectrometer, and a magnetic-bottle TOF photoelectron analyzer. The anions produced from the electrospray ionization source were guided by a radio frequency quadrupole ion guide into a 3D quadrupole ion trap, where they were accumulated for 100 ms, and then pulsed into the extraction zone of the TOF mass spectrometer. During the photoelectron spectroscopic experiment, one of the $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0-4$) ions was selected by a mass gate and decelerated before being intercepted by a probing laser beam in the photodetachment zone. The emitted photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 4-m long electron flight tube. Photoelectron TOF spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of I^- and O^- . The electron binding energy spectra presented here were obtained by subtracting the kinetic energy spectra from the detachment photon energy.
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- The origin of the X' feature was confirmed by the following facts. (1) In bare NaSO_4^- , the X' was due to $(\text{NaSO}_4)_2^{2-}$ (ref. 15). (2) We have observed $(\text{NaSO}_4)_2^{2-}(\text{H}_2\text{O})_1$ species in the mass spectra (# peak, Fig. 1 top), and verified it by its PES spectrum, which showed two bands centered at 2.4 and 4.3 eV (see the †ESI). (3) The larger $(\text{NaSO}_4)_2^{2-}(\text{H}_2\text{O})_{2n-1}$ species were also discernable in the mass spectra although they were quite weak and complicated by the neighboring $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 13, 15$) dianions.
- We have obtained the 193 nm photoelectron spectrum of this contaminant by mass-selecting this species. The recorded spectrum exhibited one intense broad band centered at ~ 3.5 eV (spanning from 2.5 to 4.5 eV), and a very weak broad feature peaked at ~ 5 eV (4.7–5.3 eV) with only a few percent intensity relative to the 3.5 eV band. The possible contribution from $\text{SO}_4(\text{H}_2\text{O})_{16}^{2-}$, which is 1 m/z higher than $\text{NaSO}_4^-(\text{H}_2\text{O})_4$, is also negligible, as confirmed from the 193 nm spectrum of $\text{SO}_4(\text{H}_2\text{O})_{16}^{2-}$ (Fig. 4 in ref. 19). The comparison among the spectra of $\text{NaSO}_4^-(\text{H}_2\text{O})_4$, $\text{SO}_4(\text{H}_2\text{O})_{16}^{2-}$, and the impurity is presented in the ESI†.
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